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THE IDENTIFICATION OF SMALL AMOUNTS OF DYESTUFFS BY OXIDATION WITH BROMIN.

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The test to aid in identifying small amounts of coloring matters, which is described in this paper, has been in use in the New York laboratory for some time. It is simple, in many cases very sensitive, and seems to require no special care to obtain reasonably dependable results.

A few cubic centimeters of the dye solution is treated with bromin water, added drop by drop until about twice as much has been used as is required to destroy the color. Some hydrazin sulphate solution is then added to take up the excess of bromin, and finally an excess of sodium carbonate. A second test portion is treated in exactly the same way, except that a few drops of α-naphthol solution (10 per cent in 50 per cent alcohol) are added just before making alkaline with the carbonate.

The behavior of some of the different classes of dyes may be indicated by typical examples, which show reactions obtained using 0.01 per cent solutions of the dyes unless otherwise indicated. Solutions of the natural coloring matters, however, were made by boiling 0.1 gram of the plant or animal tissue with 100 cc of water. The numbers after the names in the following table refer to the Green-Schultz-Julius tables.

Identification of small amounts of coloring matters.

Class.	Coloring matter.	Colorations obtained on addition of—			
		Bromin.	Hydrazin sulphate.	Sodium carbonate.	α-naphthol and sodium carbonate
Nitro	Naphthol yellow S (4).	Colorless	Colorless	Yellowish brown	Yellowish brown.
Monazo (a)	Tartrazin (94)	do	do	Colorless	Red.
Monazo (b)	New coccin (106).	Pale yellow	Pale yellow	Very pale olive	Purplish red.
	Amaranth (107).	do	Pale brownish.	Deep blue	Do.
	Fast red C (103).	do	Pale brownish to pale pink.	Bluish red	Do.

Identification of small amounts of coloring matters—Continued.

Class.	Coloring matter.	Colorations obtained on addition of—			
		Bromin.	Hydrazin sulphate.	Sodium carbonate.	α-naphthol and sodium carbonate.
Disazo	New red L (163).	Brown	Pale brownish.	Brown	Purple to brown.
Triphenyl methane.	Light green SF yellowish (435).	Pale brown	Nearly colorless.	Nearly colorless.	Nearly colorless.
Xanthene	Erythrosin (517)	Brown	Brown	Red, green fluorescence.	Red, green fluorescence.
	Rhodamin B (504).	Precipitate	....	....	
	Rhodamin B 0.002 per cent.	Colorless, then bluish red.	Bluish red	Bluish red, paler.	Bluish red, paler.
Alizarin	Alizarin red S (546).	Pale yellow	Yellow	Purplish red	Purplish red.
Azin	Safranin (584)	Precipitate	....	....	
	Safranin, 0.002 per cent.	Nearly colorless.	Red	Red	Red.
	Azocarmine G (604).	Pale greenish yellow.	....do	....do	Do.
Quinolin	Quinolin yellow.	Colorless	Yellow	Yellow	Yellow.
Natural coloring matters.	Fustic	Deep brown, then yellow.	Pale yellow	Pale brown	Pale brown.
	Saffron	Colorless	Colorless	Pale yellow	Pale yellow.
	Cochineal	Pale yellow	Pale yellow	Pale brown	Pale brown.

With the azo dyes, diazonium compounds are formed as shown by M. P. Schmidt,[1] the azo group in most cases remaining attached to the non-hydroxylated or -aminated residue (that of the diazo component). On addition of α-naphthol, followed by sodium carbonate, coupling takes place and by the solubilities of the dye formed, in ether and in amyl alcohol, and by its behavior when dyed in wool, the first component can usually be readily identified.

With some dyes, however, such as Bordeaux B and Amaranth, products are formed by the oxidation which themselves react with the diazo compound, producing colored azo derivatives. The dye thus formed from Amaranth is red in acid and blue in sodium carbonate solutions, and becomes pale brown on addition of caustic alkalies.

The monazo colors are readily attacked by bromin, the diazo colors less readily, those derived from triphenyl methane with some difficulty, and the acid flourescein dyes merely pass more or less completely into the stable bromin derivatives. In general the color should be in neutral or faintly acid solution. Hydrochloric acid, however, if not present in excessive amount, in most cases does not interfere. If much foreign matter is present, the dye should be purified by taking up with amyl alcohol and evaporating or by some similar method. A concentration of about 1 to 10,000 is quite suitable for the acid dyes. With 0.01 per cent solutions of basic dyes, precipitates are usually obtained, rather obscuring any color reactions, and more dilute solutions must be employed.

[1] J. prakt. Chem., 1912, 84: 235.

Except with dyes very readily attacked where decolorization takes place, and with a few basic coloring matters, the coloration on adding bromin is of no importance, a yellow tint being perhaps due chiefly to the excess of halogen. Chlorin water seems to give the same reactions as bromin water, but is inconvenient to prepare and offers no special advantages.

In general it may be said that if in testing unknown solutions the dye is bleached by bromin and restored by hydrazin, or if the coloration with α-naphthol and sodium carbonate is different from that with sodium carbonate alone a coal-tar color is present.

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